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HYDROGELS

Toughened up

> the gel showed a remarkable instant thermal stiffening

Conventional polymers soften above their glass transition temperature — think about familiar plastic products such as vinyl bags and PET bottles. Now Jian Ping Gong and colleagues, writing in *Advanced Materials*, present a polymer that, when temperature is raised, undergoes a reversible and rapid switching from a soft hydrogel to a rigid plastic.

The starting material is an inexpensive, nontoxic hydrogel composed of a water-containing network of poly(acrylic acid) (PAAc), the same polymer used in water-absorbing diapers. PAAc hydrogels do not normally undergo a thermal phase separation, but when the gel is immersed in an aqueous solution containing calcium acetate (a kind of salt used as a food additive) the calcium and acetate ions diffuse into the gel, forming bonds with the carboxyl groups of the polymer. The acetate moieties, which are hydrophobic, dehydrate at high temperature, strengthening the ionic bonds between the carboxyl groups and calcium ions thanks to a decrease in the relative permittivity of the environment. Such interplay between hydrophobic and ionic interaction triggers a strong dehydration of the polymer, and dehydrated domains with water trapped in between form when the temperature rises to 60°C and beyond.

Crossing the transition temperature, the material's stiffness, strength and toughness increase sharply, whereas its volume remains unchanged. The gel, from transparent and soft, becomes opaque and stiff. At 60°C, a thin gel sheet can support a 10 kg weight. This thermal hardening is reversible and can be repeated over multiple cycles.

"We discovered this phenomenon by chance," comments Takayuki Nonoyama, first author of the paper. "Our group specializes in developing tough hydrogels based on a sacrificial bond structure that preferentially ruptures under mechanical stress, dissipating large amounts of energy and therefore toughening the material." The carboxyl groups of PAAc are known to crosslink with multivalent ions through ionic bonds. Thus, the gel can be expected to toughen in the presence of calcium ions, forming ionic bonds that should serve as reversible sacrificial bonds to dissipate energy. However, the gel only showed a weak toughness increase after being immersed in a calcium chloride solution, owing to relatively weak ionic bonding.

Credit: Adrienne Bresnahan/Moment/Getty

"Then we tried calcium acetate, which resulted in stronger ionic bonds," recalls Nonoyama. "Surprisingly, the gel showed a remarkable instant thermal stiffening."

The behaviour of the system is related to the low critical solution temperature of the phase separation of the polymer. However, other hydrogels with similar low critical solution temperatures undergo a very slow phase separation, with a small stiffness change that is accompanied by a substantial volume shrinking. The different behaviour observed in the new material hints at an additional mechanism at work: the dehydration-induced glassy transition, which is specific to this hydrogel. This transition only occurs in systems with a strong phase-separation ability at high temperature, which is in turn driven by the synergetic effect of hydrophobic and ionic interactions.

This mechanism is one of the tricks nature uses to enable organisms to survive at high temperatures. "We noticed that the constitutive proteins of bacteria surviving in extreme environments, such as hot springs, have more charged residues and hydrophobic residues than those of animals living in normal environments," comments Gong. "This means that these proteins exploit the same molecular strategy as our hydrogel to remain stable at high temperature."

The material could find application for heat absorption or in protective sportswear. "It could be used for smart suits that are soft and stretchable in normal conditions, but instantly become stiff in the presence of friction heat generated in traffic or sport incidents," explains Gong. The first results, obtained on gel composites reinforced with woven glass fabrics, are promising.

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ORIGINAL ARTICLE Nonoyama, T. et al. Instant Thermal Switching from Soft Hydrogel to Rigid Plastics Inspired by Thermophile Proteins. *Adv. Mater.* https://doi.org/10.1002/adma.201905878 (2019)